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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Extrudable Methyl Methacrylate Polymer Compositions

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to improvements in or relating to polymeric compositions, in particular to polymeric compositions which are based essentially on methyl methacylate.

There is considerable interest in making extruded articles, e.g. sheets and tubes from polymethyl methacrylate or methyl methacrylate copolymers having a pimpled matt finish. As well as having a decorative effect in their own right they are also extremely useful as panels or tubes for use in lighting fittings. One method by which a matt effect can be obtained is by extruding the polymer with the temperature of the die carefully controlled so that the phenomenon known as "sharkskin" appears on the surface of the extruded article. This produces a matt effect, but it is difficult to control. Another method is to use embossed rolls. This is effective for sheet-production but cannot be used where a shaped profile is extruded. It would clearly be an advantage if articles having a pimpled matt finish could be produced by extrusion without having to depend upon control of the extrusion conditions or the use of a post extrusion operation to produce the effect.

Accordingly, the present invention provides a polymeric composition suitable for extrusion to produce articles having a pimpled matt finish which comprises a mixture of two polymers A and B, in which polymer A is either (1) a polymer of methyl methacylate with 0 to 15% of the weight of the polymer A of a monoethylenically unsaturated copolymerisable compound and has a reduced viscosity as hereinafter defined of 0.4 to 0.55, or (2) a polymer of methyl methacrylate with 0 to 6% of the weight of the polymer A of a monoethylenically unsaturated copolymerisable compound and has a reduced viscosity as hereinafter defined of 0.60 to 1.2, and polymer B is either (1) a polymer of methyl methacrylate with 0 to 15% by weight of polymer B of a monoethylenically unsaturated copolymerisable compound and has a reduced viscosity as hereinafter defined at least three times the reduced viscosity of polymer A and of a value that is at least 1.6, or (2) a copolymer of methyl methacrylate with 0 to 15% by weight of polymer B of a monoethylenically unsaturated copolymerisable compound and 0.2 to 5.0% by weight of polymer B of a copolymerisable ethylenically unsaturated compound containing at least two $CH_2=C<$ groups per molecule, and in which the mixture of A and B contains from 2 to 40% by weight of polymer B by weight of the mixture.

By the term "reduced viscosity" as used throughout this specification and claims we mean the reduced viscosity of a polymer as measured as a 1% weight/volume solution in chloroform at 20°C and experessed in decilitres/gram.

Examples of monoethylenically unsaturated compounds copolymerisable with methyl methacrylate include the following: acrylic acid and the esters of acrylic acid with saturated alcohols, particularly the alkyl esters of acrylic acid containing one to eight carbon atoms in the alkyl moiety of the ester i.e. methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl and octyl alcohols in all their isomeric forms; methacrylic acid and its alkyl esters other than methyl methacrylate; monovinyl aromatic compounds particularly styrene, α-methyl styrene, o-, m- and p-chlorostyrenes and the related bromo-, fluoro-, methyl- and

[Price 5s. 0d. (25p)]

ethyl-styrenes; acrylamide; methacrylamide; acrylonitrile; and methacrylonitrile.

Examples of compounds containing at least two $CH_2=C<$ groups per molecule and copolymerisable with methyl methacrylate include glycol dimethacrylate, triethylene glycol dimethacrylate, divinyl benzene, vinyl methacrylate, methylene dimethacrylate, allyl methacrylate, diallyl phthalate, diallyl maleate, allyl acrylate and methallyl acrylate.

It is preferred that polymer B should form from 10 to 30% by weight of the weight of the mixture of polymers A and B.

The particle size of polymer A is that normally used in extrusion grades of polymer. Thus it can be in the form of small beads of weight average particle size 50 to 1,000 mircons, or in the large cube cut form, e.g. in the form of cubes or other cut shapes with edge lengths of from 1 to 6 mms. Polymer B is preferably in the form of small beads of weight average particle size 50 to 500 mircons, more preferably 50 to 200 microns. If polymer B is finer than 50 microns, the flow properties of the composition may be affected and feeding of the composition to an extruder may consequently be difficult. On the other hand if the particle size of polymer B is greater than 500μ large lumps may form in the extrudate.

Both polymers A and B are most conveniently made by a granular polymersiation process, otherwise known as a bead or pearl process. In this process the monomer or monomers to be polymerised are dispersed by stirring in a heated autoclave which may be sealed or under reflux. Dispersion of the monomer droplets which are non-colloidal, is assisted by a granulating agent. Such compounds are well known in the polymerisation art, and include, for example, gelatin, starch, sodium polymethacrylate and hydrolysed polyvinyl acetate or maleic anhydride copolymers.

In the case of polymer B in the cross-linked form, as the proportion of the monomer containing at least two $CH_2=C<$ groups per molecule is increased so the coarseness of the matt finish of the extrudate increases. At the same time the gloss finish of the extrudate increases. Increasing the proportion of polymer B in the mixture has the effect of reducing the gloss of the extrudate and of increasing the coarseness of the matt finish.

The control of the reduced viscosity of polymers made by the known polymerisation processes is well known and can be effected, for example, by the addition to the monomer of a chain regulator or modifier such as teriary dodecyl mercaptan or lauryl mercaptan.

The control of the polymer particle size can be achieved by adjusting the stirrer speed of the polymerisation vessel.

The compositions of this invention can be used to make a large variety of extruded articles particularly sheet, having an attractive pimpled matt finish.

The invention is illustrated by the following examples in which all parts are expressed by weight.

EXAMPLE 1

A blend of two polymers A and B was prepared by dry tumbling 90 parts of polymer A and 10 parts of polymer B. Polymer A was a copolymer of 97 parts of methyl methacrylate and 3 parts of ethyl acrylate of reduced viscosity 0.50 dl./g. prepared by a granular polymerisation process and having an average particle size of 150 microns. Polymer B was a methyl methacrylate homopolymer of reduced viscosity 3.0 dl./g. prepared by a granular polymerisation process and having an average particle size of 90 microns.

The polymer blend was extruded through a slit die to form a sheet which had a matt finish and exhibited a low level of surface gloss as measured by A.S.T.M. D 523.

EXAMPLE 2

Example 1 was repeated but with polymer B having a reduced viscosity of 8.0 dl./g. A sheet having a coarse, uniform matt finish was obtained on extrusion with a surface gloss of 17% as measured by A.S.T.M. D 523. Sheet obtained by extruding polymer A alone was transparent and had a surface gloss of 50%.

EXAMPLE 3

Example 2 was repeated but using 20 parts of polymer B. The extruded sheet had a coarse, uniform matt finish, and a surface gloss of 8.5% as measured by A.S.T.M. D 523.

EXAMPLE 4

Example 1 was repeated except that polymer A had a reduced viscosity of 0.8 dl./g. Sheet extruded from the blend had a uniform, coarse matt finish.

EXAMPLE 5

A blend of two polymers A and B was prepared by dry tumbling 80 parts of polymer A with 20 parts of polymer B. Polymer A was a copolymer of 97 parts methyl methacrylate and 3 parts ethyl acrylate of reduced viscosity 0.70 dl./g. prepared by a granular polymerisation and having an average particle size of 280 microns. Polymer B was a copolymer of 97 parts methyl methacrylate, 3 parts ethyl acrylate and 0.3 parts glycol dimethacrylate, prepared by a granular polymerisation process, and having an average particle size of 80 microns and an insoluble get content in chloroform of 47% (1 part of polymer added to 100 parts of chloroform at 20°C).

Sheet extruded from the polymer blend had a coarse, uniform, matt finish.

EXAMPLES 6—15

Various blends were prepared of polymers A and B by dry tumbling and sheet obtained by extruding the blends. Polymer A was a copolymer of 97 parts of methyl methacrylate and 3 parts of ethyl acrylate prepared by a granular polymerisation process, and having a reduced viscosity of 0.7 dl./g. and an average particle size of 280 microns. Polymer B was a copolymer of 97 parts of methyl methacrylate, 3 parts of ethyl acrylate and a third monomer containing two $CH_2=C<$ groups per molecule. The nature and amounts of the third monomer are specified in the table below as are also the amounts of polymers A and B in the blends, and the surface gloss and appearance of sheets extruded from the blends.

Example	Third Monomer in Polymer B	Amount of third monomer parts	% Gel in Polymer B (1)	Parts % Polymer B in Blend	% Gloss of extruded sheet (2)	Surface texture of extruded sheet
6	Glycol Dimethacrylate	0.3	47	20	4.9	Coarse matt
7	Glycol Dimethacrylate	0.5	not measured	20	4.7	Less coarse than Example 6
8	Glycol Dimethacrylate	0.6	83	20	4.5	Fine matt
9	Glycol Diemthacrylate	0.75	88	20	5.5	Fine matt but coarser than Example 8
10	Glycol Dimethacrylate	1.0	98	10	15.0	
11	Glycol Dimethacrylate	1.0	98	20	5.8	Increasing coarseness of matt finish
12	Glycol Dimethacrylate	2.0	100	20	6.3	
13	Glycol Dimethacrylate	5.0	100	10	21.0	
14	Triethylene Glycol Dimethacrylate	1.45	89	20	4.9	Similar to Example 11
15	Divinyl Benzene	0.4	57	20	2.2	Similar to Example 6

(1) 1 part of polymer added to 100 parts of chloroform at 20°C.
(2) A.S.T.M. D523.

For comparative purposes Polymer A extruded by itself gave a clear transparent sheet with a gloss of 50%.

WHAT WE CLAIM IS:—

1. A polymeric composition suitable for extrusion to produce articles having a pimpled matt finish which comprises a mixture of two polymers A and B, in which polymer A is either (1) a polymer of methyl methacrylate with 0 to 15% of the weight of the polymer A of a monoethylenically unsaturated copolymerisable compound and has a reduced viscosity as hereinbefore defined of 0.4 to 0.55 or (2) a polymer of methyl methacrylate with 0 to 6% of the weight of the polymer A of a monoethylenically unsaturated copolymerisable compound and has a reduced viscosity as hereinbefore defined of 0.60 to 1.2, and polymer B is either (1) a polymer of methyl methacrylate with 0 to 15% by weight of polymer B of a monoethylenically unsaturated copolymerisable compound and has a reduced viscosity as hereinbefore defined at least three times the reduced viscosity of polymer A and of a value that is at least 1.6, or (2) a copolymer of methyl methacrylate with 0 to 15% by weight of polymer B of a monoethylenically unsaturated copolymerisable compound and 0.2 to 5.0% by weight of polymer B of a copolymerisable ethylenically unsaturated compound containing at least two $CH_2=C<$ groups per molecule, and in which the mixture of A and B contains from 2 to 40% by weight of polymer B by weight of the mixture.

2. A polymeric composition according to claim 1 in which polymer B forms from 10% to 30% by weight of the weight of the mixture of polymers A and B.

3. A polymeric composition according to claim 1 or claim 2 in which polymer A is in the form of small beads of weight average particle size 50 to 1000 microns.

4. A polymeric composition according to any of the preceding claims in which polymer B is in the form of beads of weight average particle size 50 to 500 microns.

5. A polymeric composition according to claim 4 in which polymer B is in the form of beads of weight average particle size 50 to 200 microns.

6. A polymeric composition according to any of the preceding claims in which one of the monoethylenically unsaturated compounds copolymerised with methyl methacrylate comprises acrylic acid or an ester thereof.

7. A polymeric camposition according to claim 6 in which the ester of acrylic acid is an alkyl ester containing from one to eight carbon atoms in the alkyl moiety of the ester.

8. A polymeric composition according to any of claims 1 to 5 in which one of the monoethylenically unsaturated compounds copolymerised with methyl methacrylate comprises a monovinyl aromatic compound.

9. A polymeric composition according to any of the preceding claims in which, when present, the compound containing at least two $CH_2=C<$ groups per molecule comprises glycol dimethacrylate.

10. A polymeric composition according to any of claims 1 to 8 in which, when present, the compound containing at least two $CH_2=C<$ groups per molecule comprises triethylene glycol dimethacrylate.

11. Polymeric compositions substantially as hereinbefore described with particular reference to the accompanying examples.

12. Extruded articles having a pimpled matt finish whenever prepared from a polymeric composition according to any of the preceding claims.

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